

## CLAIMS

What is claimed is:

1. A method of making a catalyst for use in oligomerizing an olefin, comprising a chromium-containing compound, a pyrrole-containing compound, a metal alkyl, a halide-containing compound, and optionally a solvent the method comprising abating all or a portion of water, acidic protons, or both from a composition comprising the chromium-containing compound, a composition comprising the pyrrole-containing compound, a composition comprising a non-metal halide-containing compound, a composition comprising the solvent, or combinations thereof prior to contact thereof with a composition comprising a metal halide-containing compound.
2. The method of claim 1, wherein the composition comprising a metal halide-containing compound comprises (i) a metal alkyl halide, (ii) a metal halide and a metal alkyl, (iii) a non-metal halide and a metal alkyl, or (iv) combinations thereof.
3. The method of claim 1, further comprising use of catalyst comprising abated components yields less of one or more corrosive compounds than use of the same catalyst without abated components.
4. The method of claim 1, wherein the abating all or a portion of water, acidic protons, or both further comprises contacting one or more of the compositions comprising water, acidic protons, or both and a non-halide metal alkyl prior to contact thereof with the composition comprising the metal halide-containing compound.
5. The method of claim 4, wherein the non-halide metal alkyl comprises triethylaluminum (TEA).

6. The method of claim 4, wherein the portion of the non-halide metal alkyl is an amount effective to abate substantially all available water, acidic protons, or both from the compositions contacted with the non-halide metal alkyl.
7. The method of claim 4, wherein the acidic protons are provided by 2-ethylhexanoic acid.
8. The method of claim 4, wherein the non-halide metal alkyl is added in an amount less than or equal to about 30 weight percent of the total weight of the contacted compositions.
9. The method of claim 4, wherein the abating all or a portion of water, acidic protons, or both further comprises forming a mixture by contacting the composition comprising the chromium-containing compound and the non-halide metal alkyl prior to contacting the mixture with the remaining compositions.
10. The method of claim 9, wherein the non-halide metal alkyl is added to the composition comprising the chromium-containing compound to form the mixture.
11. The method of claim 9, wherein the non-halide metal alkyl is added in an amount such that the molar ratio of non-halide metal alkyl to chromium-containing compound in the mixture is less than about 1:1.
12. The method of claim 9, wherein the non-halide metal alkyl is added in an amount sufficient to abate at least about 25 percent of the water, acidic protons, or both.
13. The method of claim 9, wherein the non-halide metal alkyl is added in an amount that is about a 200 percent excess of an amount sufficient to abate at least about 100 percent of the water, acidic protons, or both.
14. The method of claim 9, further comprising filtering a precipitate from the mixture prior to combining the mixture with the composition comprising the pyrrole-containing compound, the

composition comprising the halide-containing compound, the composition comprising the solvent, any remaining non-halide metal alkyl, or combinations thereof.

15. The method of claim 9, further comprising contacting the composition comprising the pyrrole-containing compound with the composition comprising the chromium-containing compound prior to said contacting the composition comprising the chromium-containing compound with the non-halide metal alkyl.

16. The method of claim 15, wherein the non-halide metal alkyl is added to the combination of the composition comprising the chromium-containing compound and the composition comprising the pyrrole-containing compound.

17. The method of claim 4, wherein the abating all or a portion of water, acidic protons, or both further comprises contacting the composition comprising the pyrrole-containing compound with all or a portion of the non-halide metal alkyl to form a mixture prior to contacting the mixture with the remaining compositions.

18. The method of claim 9, wherein the abating all or a portion of water, acidic protons, or both further comprises combining the composition comprising the pyrrole-containing compound with all or a portion of the non-halide metal alkyl to form a second mixture prior to contacting the second mixture with the remaining compositions.

19. The method of claim 4, wherein the contacting further comprises:

(a) contacting the composition comprising the chromium-containing compound and the composition comprising the pyrrole-containing compound;

(b) contacting the resultant contacted compounds from step (a) and the non-halide metal alkyl; and

(c) contacting the resultant contacted compounds from step (b) and the composition comprising the metal halide-containing compound.

20. The method of claim 19, further comprising contacting a non-metal halide with (i) the composition comprising the chromium-containing compound prior to step (a), (ii) the composition comprising the pyrrole-containing compound prior to step (a), (iii) both the composition comprising the chromium-containing compound and the composition comprising the pyrrole-containing compound prior to step (a); or (iv) the resultant contacted compounds from step (a);

21. The method of claim 4, wherein:

(a) the composition comprising the chromium-containing compound and a portion of the non-halide metal alkyl are contacted to form a first mixture;

(b) the composition comprising the pyrrole-containing compound and a portion of the non-halide metal alkyl are contacted to form a second mixture; and

(c) the first mixture and the second mixture are contacted with the composition comprising metal halide-containing compound.

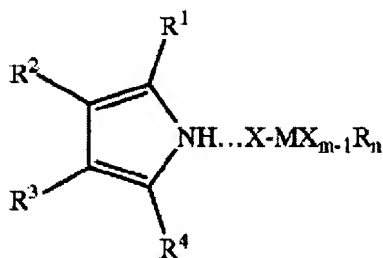
22. The method of claim 21, wherein step (c) is performed over a period of time, a starting pyrrole:Cr molar ratio at the start of the period of time is greater than the final pyrrole:Cr molar ratio of the catalyst, and an ending pyrrole:Cr molar ratio at the end of the period of time is less than the final pyrrole:Cr molar ratio of the catalyst.

23. A process for preparing a chromium-based catalyst, comprising bringing a pyrrole ring-containing compound, an alkyl aluminum compound, and a halogen-containing compound into contact with each other in a hydrocarbon solvent, halogenated hydrocarbon solvent or mixture thereof, and then bringing the mixed resultant solution into contact with the chromium compound,

wherein water, acidic protons, or both are abated from the catalyst or a component thereof prior to or during preparation of the catalyst.

24. A process for preparing a chromium-based catalyst, comprising bringing a chromium compound, a pyrrole ring-containing compound, an alkyl aluminum compound, and a halogen-containing compound into contact with each other in a hydrocarbon solvent, halogenated hydrocarbon solvent or mixture thereof in the absence of alpha-olefin under such a condition that the concentration of the chromium compound in the resultant mixed solution is about  $1 \times 10^{-7}$  to 1 mol/liter, wherein water, acidic protons, or both are abated from the catalyst or a component thereof prior to or during preparation of the catalyst.

25. A process for treating a catalyst component, comprising abating water, acidic protons, or both from a catalyst component comprising a pyrrole derivative represented by the general formula (I):



(I)

wherein R<sup>1</sup> to R<sup>4</sup> are a hydrogen atom or a linear or branched hydrocarbon group having 1 to 20 carbon atoms, in which R<sup>3</sup> and R<sup>4</sup> may integrally form a ring; X is a halogen atom; M is an element selected from the group consisting of those belonging to 3-Group, 4-Group, 6-Group (exclusive of chromium), 13-Group, 14-Group and 15-Group of the Periodic Table; m and n are numbers satisfying the relationships of  $1 \leq m \leq 6$ ,  $0 \leq n \leq 5$  and  $2 \leq m+n \leq 6$  with the proviso that the sum of m and n is identical to the valence of the element M; n represents the number of Rs;

and R is a hydrogen atom or a linear or branched hydrocarbon group having 1 to 20 carbon atoms and when n is not less than 2, and Rs may be the same or different.

26. A catalyst for trimerization of ethylene which comprises:

(i) an organometallic complex having a neutral multidentate ligand having a tripod structure, represented by the following formula (1):



wherein A is a neutral multidentate ligand having a tripod structure, M is a transition metal atom of group 3 to group 10 of the periodic table, each Q is independently selected from the group consisting of a hydrogen atom, a halogen atom, a straight chain or branched alkyl group having 1 to 10 carbon atoms which may have a substituent, an aryl group having 6 to 10 carbon atoms which may have a substituent, and n is an integer equal to a formal oxidation valence of M, and

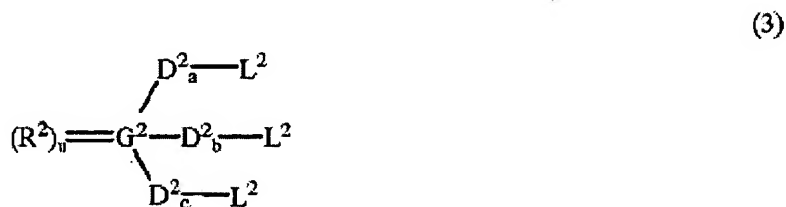
(iv) an alkylaluminoxane;

said neutral multidentate ligand A in formula (1) being a tridentate ligand represented by the following formula (2) or formula (3):



wherein j, k and m independently represent an integer of 0 to 6, each  $D^I$  independently represents a divalent hydrocarbon group which may have a substituent, each  $L^I$  independently represents a substituent containing an element of group 14, 15, 16 or 17 of the periodic table, with the proviso

that all of the three  $L^1$ 's are not concurrently a substituent containing an element of group 14 or 17,  $G^1$  represents a carbon or silicon atom, and  $R^1$  represents a hydrogen atom, an alkyl group having 1 to 10 carbon atoms which may have a substituent, or an aryl group having 6 to 10 carbon atoms which may have a substituent;



wherein a, b and c independently represent an integer of 0 to 6; u represents an integer of 0 or 1; each  $D^2$  independently represents a divalent hydrocarbon group which may have a substituent; each  $L^2$  independently represents a substituent containing an element of group 14, 15, 16 or 17 of the periodic table, with the proviso that all of the three  $L^2$ 's are not concurrently a substituent containing an element of group 14 or 17,  $G^2$  represents a nitrogen or phosphorus atom when u is 0, or a phosphorus atom when u is 1, and  $R^2$  represents an oxygen or sulfur atom, wherein water, acidic protons, or both are abated from the catalyst or a component thereof prior to or during formation of the catalyst.

27. The catalyst of claim 26, further comprising a halogenated inorganic compound.

28. The catalyst of claim 27, further comprising an alkyl group-containing compound represented by the following formula (4):



wherein p and q are numbers satisfying the formulae:  $0 < p \leq 3$  and  $0 \leq q < 3$ , provided that (p+q) is in the range of 1 to 3, E represents an atom, other than a hydrogen atom, of group 1, 2, 3, 11, 12 or 13 of the periodic table, each R independently represents an alkyl group having 1 to 10 carbon

atoms, and each J independently represents a hydrogen atom, an alkoxide group having 1 to 10 carbon atoms, an aryloxy group having 6 to 10 carbon atoms, an aryl group having 6 to 10 carbon atoms or a halogen atom.

29. The catalyst of claim 26, further comprising an alkyl group-containing compound represented by the following formula (4):



wherein p and q are numbers satisfying the formulae:  $0 < p \leq 3$  and  $0 \leq q < 3$ , provided that (P+q) is in the range of 1 to 3, E represents an atom, other than a hydrogen atom, of group 1, 2, 3, 11, 12 or 13 of the periodic table, each R independently represents an alkyl group having 1 to 10 carbon atoms, and each J independently represents a hydrogen atom, an alkoxide group having 1 to 10 carbon atoms, an aryloxy group having 6 to 10 carbon atoms, an aryl group having 6 to 10 carbon atoms or a halogen atom.

30. The catalyst of claim 26, further comprising at least one compound selected from the group consisting of an amine compound and an amide compound.

31. A catalyst system for the oligomerization of olefins, the catalyst system including:

a chromium source;

a metal alkyl; and

a halopyrrole ligand, wherein water, acidic protons, or both are abated from the catalyst system or a component thereof prior to or during formation of the catalyst.

32. A method of producing 1-hexene including at least the step of trimerizing ethylene using a catalyst system comprising a combination of at least a chromium source, a metal alkyl and a halopyrrole ligand, wherein water, acidic protons, or both are abated from the catalyst system or a component thereof prior to or during formation of the catalyst.



33. A multidentate mixed heteroatomic ligand for an oligomerization of olefins catalyst, which ligand includes at least three heteroatoms of which at least one is a sulfur atom wherein water or acidic protons, or both are abated from the catalyst system or a catalyst component.

34. A ligand as claimed in claim 33, wherein water or acidic protons, or both are abated from the ligand, and the ligand is selected from the following types:

(a)  $R^1A(R^2BR^3)(R^4CR^5)$  wherein  $R^1$ ,  $R^3$  and  $R^5$  may be hydrogen or independently be selected from the groups consisting of alkyl, aryl, aryloxy, halogen, nitro, alkoxycarbonyl, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, or derivatives thereof, or aryl substituted with any of these substituents;  $R^2$  and  $R^4$  may be the same or different and are  $C_1$  to about  $C_{15}$  hydrocarbyls; A is nitrogen or phosphorous; and B and C are sulfur; and

(b)  $R^1A(R^2BR^3R^4)(R^5CR^6)$  wherein  $R^1$ ,  $R^3$ ,  $R^4$ , and  $R^6$  may be hydrogen or independently be selected from the groups consisting of alkyl, aryl, aryloxy, halogen, nitro, alkoxycarbonyl, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, or derivatives thereof, or aryl substituted with any of these substituents;  $R^2$  and  $R^5$  may be the same or different and are  $C_1$  to about  $C_{15}$  hydrocarbyls; A and B are individually nitrogen or phosphorous; and C is sulfur; and

(c)  $A(R^1BR^2R^3)(R^4CR^5)$  wherein  $R^2$ ,  $R^3$ , and  $R^5$  may be hydrogen or independently be selected from the groups consisting of alkyl, aryl, aryloxy, halogen, nitro, alkoxycarbonyl, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, or derivatives thereof, or aryl substituted with any of these substituents;  $R^1$  and  $R^4$  may be the same or different and are  $C_1$  to about  $C_{15}$  hydrocarbyls; B is nitrogen or phosphorous; and A and C are sulfur; and

(d)  $A(R^1BR^2R^3)(R^4CR^5R^6)$  wherein  $R^2$ ,  $R^3$ ,  $R^5$ , and  $R^6$  may be hydrogen or independently be selected from the groups consisting of alkyl, aryl, aryloxy, halogen, nitro, alkoxycarbonyl, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, or derivatives thereof, or aryl

substituted with any of these substituents;  $R^1$  and  $R^4$  may be the same or different and are  $C_1$  to about  $C_{15}$  hydrocarbyls; B and C are individually nitrogen or phosphorous; and A is sulfur.

35. A mixed heteroatomic ligand for an oligomerization of olefins catalyst, which ligand includes at least three heteroatoms, of which at least one heteroatom is nitrogen and at least two heteroatoms are not the same wherein water or acidic protons, or both are abated from the catalyst system or a catalyst component.

36. A ligand as claimed in claim 35, wherein water or acidic protons, or both are abated from the ligand, and the ligand has the structure  $R^1A(R^2BR^3R^4)(R^5CR^6R^7)$  wherein  $R^1$ ,  $R^3$ ,  $R^4$ ,  $R^6$  and  $R^7$  may be hydrogen or independently be selected from the groups consisting of alkyl, aryl, aryloxy, halogen, nitro, alkoxycarbonyl, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, or derivatives thereof, or aryl substituted with any of these substituents;  $R^2$  and  $R^5$  are the same or different and are  $C_1$  to about  $C_{15}$  hydrocarbyls; and at least A, B or C is nitrogen with the remainder of A, B and C being individually nitrogen or phosphorous.

37. The method of claim 1, wherein all or a portion of the water is removed from the chromium-containing compound prior to contact with the metal halide-containing compound.

38. The method of claim 1, wherein all or a portion of the water is removed from the chromium-containing compound prior to contact with the metal alkyl-containing compound.

39. The method of claim 37, wherein the chromium-containing compound is contacted with a solvent to form a solution and the solution is subjected to an azeotropic distillation.

40. The method of claim 39, wherein the solvent comprises an aromatic compound, halogenated compound, a paraffin, or combinations thereof.

41. The method of claim 40, wherein the aromatic compound comprises benzene, toluene, ethylbenzene, mixed xylenes, ortho-xylene, meta-xylene, para-xylene, or combinations thereof.

42. The method of claim 39, wherein the amount of water removed is monitored by infrared analysis or other known methods used to determine water content.
43. The method of claim 1, wherein one or more catalyst components other than (i) a composition comprising a metal alkyl halide, (ii) a composition comprising a metal halide and a metal alkyl, (iii) a composition comprising a non-metal halide and a metal alkyl, or (iv) combinations thereof are contacted with an adsorbent to remove water.
44. The method of claim 1, wherein the chromium-containing compound, the pyrrole-containing compound, the non-metal halide-containing compound, the solvent, or combinations thereof is contacted with an adsorbent to remove water.
45. The method of claim 44, wherein the adsorbent comprises a 3-Angstrom molecular sieve, a 5-Angstrom molecular sieve, alumina, silica, or combinations thereof.